DEVELOPMENT OF STEAM HYDROGASIFICATION PROCESS DEMONSTRATION UNIT-5 LB/HR PDU DESIGN REPORT

Prepared for: California Energy Commission
Prepared by: University of California

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ACKNOWLEDGEMENTS

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PREFACE

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- Transportation

"Development of Steam Hydrogasification Process Demonstration Unit-5 lb/hr PDU Design Report" is the final report for the Hydrogasification Process project contract number 500-09-008 conducted by the University of California. The information from this project contributes to Energy Research and Development Energy-Related Environmental Research Program.

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ABSTRACT

The increasing cost of transportation fuel along with increasing concerns about greenhouse gas emissions globally, including California, underlies a critical need to develop sustainable alternative transportation fuels. California needs to produce nearly 2.4 billion gasoline gallon equivalents per year of alternative transportation fuels in order to meet the State Alternative Fuels Plan 2017 petroleum reduction objectives. Currently, California imports more than 95 percent of the biofuels it uses. Ramping up in-state biofuel production without competing with existing cropland will be difficult unless other, non-crop biomass resources can be used. Thermochemical production of alternative transportation fuels such as substituted natural gas, synthetic diesel or synthetic gasoline derived from renewable sources offers a viable solution for addressing these concerns. This project successfully demonstrated steam hydrogasification reaction technology using co-mingled biosolids and biomass as the feedstock in a laboratory scale process demonstration unit. The steam hydrogasification technology was able to produce various forms of energy products from carbonaceous resources. The researchers also completed a preliminary modeling evaluation and design for a pilot plant with a capacity of five tons per day using the process demonstration unit technology. The plant design included a block flow diagram with process mass, energy balance and process and utility flow diagrams. In addition, the researchers conducted preliminary economic analyses for a 3,500 bone dry tone per day substituted natural gas plant using biosolid and green waste as feedstock. The authors concluded that the results of this project warranted moving forward with plans for a demonstration pilot plant at a waste treatment facility.
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EXECUTIVE SUMMARY

Introduction
The increasing cost of transportation fuel along with increasing concerns about greenhouse gas emissions globally, including California, underlies a critical need to develop sustainable alternative transportation fuels. California needs to produce nearly 2.4 billion gasoline gallon equivalents per year of alternative transportation fuels in order to meet the State Alternative Fuels Plan 2017 petroleum reduction objectives. Currently, California imports more than 95 percent of the biofuels it uses. Ramping up in-state biofuel production without competing with existing cropland will be difficult unless other, non-crop biomass resources can be used. Thermochemical production of alternative transportation fuels such as substituted natural gas (SNG), synthetic diesel or synthetic gasoline derived from renewable sources offers a viable solution for addressing these concerns.

Project Purpose
The goals of this project were to demonstrate steam hydrogasification reaction (SHR) technology using co-mingled biosolids and biomass as the feedstock in a laboratory scale process demonstration unit (PDU) and to provide a preliminary modeling evaluation and design pilot scale facility with a capacity of five tons per day.

Project Results
An SHR reactor was developed at the University of California, Riverside (UCR) that could produce various forms of energy products from carbonaceous resources. The reactor could handle wet feedstock without drying, did not require expensive oxygen plants and operated at lower temperature than any other conventional gasification process. Each of these properties offered an advantage compared to other thermochemical gasification processes. The demonstration of the SHR technology showed it was the most efficient and economic thermochemical gasification process when compared with other existing technologies.

The PDU was designed, fabricated and operated in the UCR gasification laboratory. A steam methane reforming (SMR) reactor was integrated with the PDU to maximize synthesis gas production. The efficient production of synthesis gas at a temperature range of 650-750 degrees centigrade (°C), an ethylene (H2/C) mole ratio of 1.0, and water/feedstock mass ratio of two was demonstrated. These initial conditions were determined based on batch scale tests and the ASPEN simulation results. ASPEN is a FORTRAN-based deterministic steady-state chemical process simulator developed by the Massachusetts Institute of Technology (MIT) for the Department of Energy (DOE) to evaluate synthetic fuel technologies. It was found that under these conditions SNG can be produced at the rate of 1.2 gigajoules (GJ) per day from a feedstock flow rate of 0.1 tons per day.

A preliminary design of a pilot plant with a capacity of five tons per day was completed. A block flow diagram with process mass and energy balance and process and utility flow diagrams was developed.
In addition, preliminary process economic analyses were completed for a 3,500 bone dry tonne (BDT) per day substituted natural gas (SNG) plant using biosolid and green waste as feedstock. It was estimated that the SNG production cost is 4.39 per million British thermal units (BTUs) with an internal rate of return (IRR) of 16.68 percent. Feedstock cost and feedstock delivery cost were not taken into consideration and the economic results should be considered highly uncertain. Nevertheless, this initial economic analysis provided considerable confidence for moving forward with the pilot plant design and evaluation.

The authors concluded that the results of this project warranted moving forward with plans for a demonstration pilot plant at a waste treatment facility.

Project Benefits
This project demonstrated that steam hydrogasification technology could produce various forms of energy from renewable resources that could be used as alternative transportation fuels. If this technology is successfully demonstrated at a pilot plant, it could contribute toward meeting California’s State Alternative Fuels Plan 2017 objectives. Increased use of alternative transportation fuels will help reduce greenhouse gas emissions that contribute to climate change.
Chapter 1: Introduction

California needs to produce nearly 2.4 billion gasoline gallon equivalents per year of alternative transportation fuels in order to meet the State Alternative Fuels Plan 2017 petroleum reduction objectives. Currently, California imports more than 95 percent of the biofuels used in-state. Ramping up in-state biofuel production without competing with existing cropland will be difficult unless other, non-crop biomass resources can be used.

A recent California biomass availability assessment found that California generates approximately 83 million dry tons of biomass wastes per year creating various unresolved waste disposal issues for agricultural and forestry biomass residue streams. In addition, there are large volumes of biosolids resulting from statewide wastewater treatment facilities. There is approximately 32.1 million dry tons of biomass available every year for fuel production when sustainability and harvesting efficiency factors are considered. Further research and development is required to establish commercially-viable waste-to-energy conversion technologies that can simultaneously contribute supplies of renewable transportation fuels and reduce statewide levels of waste going to landfills. Biosolids, municipal wastes and other carbonaceous wastes are important sources of renewable carbon that are very under-utilized. Using such feedstock will yield transportation fuels with low net fuel cycle emissions while helping mitigate the disposal problems associated with these materials. Typically, these feedstocks do not lend themselves to large capacity commercial facilities because the feedstock amounts needed are seldom available within a reasonable transportation distance. In addition, these feeds typically contain a significant amount of moisture that must be dried or processed along with the feed. Hence, technologies used to process these feeds must be commercially viable in smaller scales and also be able to accommodate diverse, local feedstocks including wet carbonaceous matter.

This project is to develop a promising new waste-to-energy technology based on the Steam Hydrogasification Reaction (SHR), which has undergone several years of laboratory-scale research and development by the University of California (UC) Riverside, College of Engineering, Center for Environmental Research and Technology (CE-CERT). A Process Demonstration Unit (PDU) of the SHR process has been designed, built and operated at the CE-CERT facilities under this project. A gas cleanup system was also demonstrated to remove contaminants from the product of the SHR to supply a clean output gas to a Steam Methane Reformer (SMR). The primary feedstock for this demonstration was biosolids from the City of Riverside wastewater treatment system co-mingled with biomass (green woody waste) diverted from a local landfill. The primary product was a mixture of hydrogen and carbon monoxide (aka syngas), which can be converted into sustainable liquid transportation fuels with downstream fuel processing technology (diesel, gasoline, and jet fuel). An important partner in this project was the City of Riverside who provided the green waste and biosolids.
Chapter 2: Project Deliverables

2.1 Goals of agreement

The goals of this agreement are to:

- Demonstrate and validate a feedstock pretreatment system to produce a pumpable slurry from the comingled biomass/biosolids feedstock that will be used in the SHR process, achieving a feedstock supply rate of 0.1 ton per day (10 pounds per hour) for 24 hours of continuous operation.
- Demonstrate and validate the SHR process for the efficient conversion of the biomass and biosolids slurry produced by the pretreatment system into a producer gas, in an SHR reactor processing 0.1 ton per day (10 pounds per hour) of feedstock.
- Demonstrate and validate the syngas cleanup system and SMR that remove the contaminants from the producer gas and convert it into syngas of adequate quality to support SMR operation (as specified further in the Technical Performance Objectives).
- Complete the basic engineering design for a 5 tons/day scale pilot plant using key information obtained through the PDU demonstration.

2.2 Technical Performance Objectives

The objectives of this agreement are to:

1. (Task #2) Validate the performance and product quality of the feed pretreatment process of the PDU under the optimum conditions. The target specifications for the product composition are:
   a) Rheological Properties
      - Solid loading of the slurry >30%
      - Viscosity < 1 centi P
   b) Material Loss
      - CO₂: < 10 Vol%
      - C1–C6: < 500 ppmv

2. (Task #3) Validate the production and quality of producer gas from the SHR process of PDU under the optimum operating conditions. The target specifications for the producer gas composition are:
   a) Producer Gas Yield and Energy Content
      - Yield (dry basis) >1200 kg / ton of feed
      - Energy content of the producer gas (HHV) >15GJ/ ton of feed
   b) Producer Gas Composition – dry basis (pre clean-up)
      - H₂: 55-70 Vol%
      - CO: 5-20 Vol%
      - CH₄: 5-20 Vol%
      - CO₂: < 25 Vol%
      - Tars: < 3 mg/m³
3. (Task #4) Validate the production and quality of syngas from the combined SHR, gas cleanup and SMR units of the PDU under the optimum operating conditions. The target specifications for the producer gas composition are:

   a) Syngas Production and Energy Content
      - Syngas yield (dry basis) >1200 kg/ton of feed
      - Energy content at ambient conditions (HHV) >12 GJ/ton of feed

   b) Syngas Composition – dry basis (post clean-up)
      - H₂: 50-80 Vol%  
      - CO: 15-30 Vol%  
      - CH₄: < 5 Vol%  
      - CO₂: 5-20 Vol%  
      - Tars/Waxes: < 0.05 mg/m³  
      - Sulfur: < 0.01 ppm

4. (Task #5) Develop the basic engineering design of the 5 tons per day pilot plant to be sited at the wastewater treatment facility in Riverside, CA or at another city site. This basic engineering design of the pilot plant will allow both technical and economic feasibility analysis of a commercial scale process. The design of the pilot plant shall contain the following deliverables.
   - Block Flow Diagram
   - Process & Utility Flow Diagrams
   - Heat & Mass Balances
   - Plant Layouts & Equipment Arrangement Plan
   - Equipment, Vessel Specification / List - Long Lead Item List
   - Estimated Project Cost

2.3 Deliverables of Technical Tasks

Table 2-1 in below summarizes the outcome of the project performance to show whether project deliverables of the technical tasks, which originally set by the contract, were attained together with the section to which outcome is described in details.

<table>
<thead>
<tr>
<th>Task #</th>
<th>Deliverables</th>
<th>Section in this Report</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>• Pretreatment Process Test Plan</td>
<td>Section 3.1</td>
</tr>
<tr>
<td></td>
<td>• Batch Unit Process Design Flowsheet</td>
<td>Appendix A-B</td>
</tr>
<tr>
<td></td>
<td>• Optimum Process Conditions Report</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Continuous Unit Process Design Flowsheet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Final Pretreatment Process Test Report</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>• Steam Hydrogasification Process Demonstration Test Plan Report</td>
<td>Section 3.2-3.6</td>
</tr>
<tr>
<td></td>
<td>• SHR Detailed Design Flowsheet</td>
<td>Section 5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Appendix C, D, E</td>
</tr>
<tr>
<td>Task #</td>
<td>Deliverables</td>
<td>Section in this Report</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
</tbody>
</table>
| 4      | • Process Mass and Energy Balance Report  
        • Process Performance Results Report  
        • SHR with Gas Cleanup and SMR Demonstration Plan Report  
        • Gas Cleanup Process Detail Design Flowsheet  
        • SMR Process Detail Design Flowsheet  
        • SHR, Gas Cleanup and SMR Integrated Operation Results Report | Section 3.7  
        Section 5.1  
        Table 5.1                                             |
| 5      | • Block Flow Diagram with Process Mass and Energy Balance of Pilot Plant  
        • Process & Utility Flow Diagrams for Pilot Plant  
        • Plant Layouts & Equipment Arrangement Plan Diagram for Pilot Plant  
        • Equipment, Vessel Specification, List-Long Lead Item List for Pilot Plant and Bill  
        • of Material  
        • Final Project Report                                                                 | Section 6  
        Appendix F, G                               |
Chapter 3: PDU design

3.1 Feedstock Pretreatment Unit

Previous research reveals that the feeding of biomass feedstock, such as wood wastes and biosolids, into a pressurized reactor poses technical challenges. Conventional methods of feeding materials into a pressurized gasifier, such as screw feed and locker hoper, are unreliable and operationally expensive. To handle and transport biomass feedstocks in a cost and energy efficient manner, a pumpable slurry of biomass feedstocks with high energy and carbon content is much more favorable. Additionally, the high moisture content in biomass also favors a wet feeding method. Biomass slurries are not formed by simply mixing the wood wastes and biosolids. There are two reasons for this: 1) the low energy and carbon content in wood wastes and biosolids, 2) hygroscopic and hydrophilic nature of wood wastes. In order to prepare pumpable wood wastes and biosolids slurries with high energy and carbon content, a pre-processing step has to be implemented. This has been achieved by using a Hydrothermal Pretreatment (HTP) process developed by our research group.

The HTP system assembly, shown in Figure 3-1(a) will be operated in the stirred batch configuration. The hydrothermal reactor with temperature and pressure transducer, controller, 3 zone electric heater, serpentine cooling coil and coolant recycling system were designed by our research team and fabricated by Parr Instrument Company. The system controller box, magnetic stirrer with electric motor and the pneumatic lift support frame were designed and fabricated by Parr Instrument Company.

The hydrothermal reactor is made of 316-stainless steel. chosen because of its high nickel and molybdenum concentration and the resultant corrosive resistance to sulfuric, phosphoric, and acetic acids. Preliminary test results from a mini batch HTP reactor showed slight acidity of the slurry products (pH 3 to 4), which is mainly due to acetic acid produced from the wood wastes and biosolids. The hydrothermal reactor has a volumetric capacity of 5 gallons. A magnetic stirrer which is powered by an electric motor is implemented to rotate the agitator inside. The reactor is heated by a 3 zone electric heater jacket, as shown in Figure 3-1. A serpentine cooling coil with a coolant circulating system is implemented to transfer heat out of the hydrothermal reactor, as shown in Figure 3-2. The hydrothermal reactor assembly was installed in the CE-CERT gasification laboratory with calibration gas, coolant supply and power cord installation. A computer assisted control system with remote control software, provided by Parr Instruments, was connected to the hydrothermal slave box controller. The further details of the HTP system description can be found in the APPENDIX section of the report.
3.2 Feed Pump Design

High pressure pumps are used in a wide range of industrial and residential applications. They can be used for domestic, commercial, industrial and agricultural services and municipal water...
and wastewater services. Pumps are divided into two fundamental types based on the manner in which they transmit energy to the pumped media: dynamic or positive displacement. The type of pump is shown in Figure 3-3. Fluid properties, end use requirements, and environmental conditions should be considered while choosing pump [2].

**Figure 3-3: Type of pumps branch structure**

```
Pumps
  Dynamic
    Centrifugal
  Others (e.g. Impulse, Buoyancy)
    Special effect
  Positive Displacement
    Rotary
      Internal gear
    External gear
    Lobe
    Slide vane
```

**Fluid Properties**

The properties of the fluids being pumped can significantly affect the choice of pump. Key considerations include:

- **Acidity/alkalinity (pH) and chemical composition.** Corrosive and acidic fluids can degrade pumps, and should be considered when selecting pump materials.
- **Operating temperature.** Pump materials and expansion, mechanical seal components, and packing materials need to be considered with pumped fluids that are hotter than 200°F.
- **Solids concentrations/particle sizes.** When pumping abrasive liquids such as industrial slurries, selecting a pump that will not clog or fail prematurely depends on particle size, hardness, and the volumetric percentage of solids.
• **Specific gravity.** The fluid specific gravity is the ratio of the fluid density to that of water under specified conditions. Specific gravity affects the energy required to lift and move the fluid, and must be considered when determining pump power requirements.

• **Vapor pressure.** A fluid’s vapor pressure is the force per unit area that a fluid exerts in an effort to change phase from a liquid to a vapor, and depends on the fluid’s chemical and physical properties. Proper consideration of the fluid’s vapor pressure will help to minimize the risk of cavitation.

• **Viscosity.** The viscosity of a fluid is a measure of its resistance to motion. Since kinematics viscosity normally varies directly with temperature, the pumping system designer must know the viscosity of the fluid at the lowest anticipated pumping temperature. High viscosity fluids result in reduced centrifugal pump performance and increased power requirements. It is particularly important to consider pump suction-side line losses when pumping viscous fluids.

*End Use Requirements — System Flow Rate and Head*

From the product of the HTP system, typical fluid characteristics was investigated and summarized in Table 3-1.

**Table 3-1: Properties and flow rate of fluid**

<table>
<thead>
<tr>
<th>Product</th>
<th>Content</th>
<th>nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of fluid</td>
<td>Biosoid (DAFT) with Biomass</td>
<td></td>
</tr>
<tr>
<td>Product temperature</td>
<td>°C</td>
<td>25</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>Approx.</td>
<td>1.2</td>
</tr>
<tr>
<td>Particle size</td>
<td>μm</td>
<td>&lt;150</td>
</tr>
<tr>
<td>PH value</td>
<td>Approx.</td>
<td>5-7</td>
</tr>
<tr>
<td>Solid content (w/w)</td>
<td>Approx.</td>
<td>%TS 40</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>Approx.</td>
<td>CPS 1000</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>PSI</td>
<td>N/A</td>
</tr>
<tr>
<td>Flow rate</td>
<td>L/hour</td>
<td>15-20</td>
</tr>
</tbody>
</table>

Based on the properties of fluid and flow rate, progressive cavity pump, belonging to positive displacement pumps, was recommended. A progressive cavity type pump was chosen since it has no pulsating and delivers a more even flow. Progressive cavity pump have many applicationsin industrial processes, construction, wastewatertreatment, oil field service, pulp and paper processes, and food processing.

Advantages of progressive cavity pump:

• Wide range of flows and pressures.

• Wide range of liquids and viscosities

• Low internal velocities.
• Self-priming, with good suction characteristics.
• High tolerance for entrained air and gases.
• Minimum churning or foaming.
• Pulsation-free flow and quiet operation.
• Rugged design — easy to install and maintain.
• High tolerance to contamination and abrasion.

For the selection of specific type of the progressive cavity pump, MEMO pump (N-ELOR NM015BO02S12B) provided by METZSCH Pumps North America Company was designed to be used for PDU pump design. In order to solve the problem of settling of slurry produced by pretreatment process, the slurry will be mixed in the tank before going into pump. The further detailed technical parameters of pump used in the PDU are given in APPENDIX C.

3.3 H₂ supply source

Evaluation of hydrogen supply system for steam hydrogasification is part of development of PDU process. This section describes the design of hydrogen supply method. Amount of hydrogen required in the SHR process are given in Table 3-2. These values were obtained from the “SHR Detailed Design Flow-sheet” and “Process Mass and Energy Balance Report” which were the deliverable of the Task#3 of the program. Consumption of H₂ was estimated to 178.6ft³/hour, 5715ft³/week or 22860ft³/month.

There are three options; 1) industrial grade H₂ supply system including gas cylinders (6 pack or 12 pack); 2) bulk hydrogen tank (trailer or skid) and 3) hydrogen generator. These options are compared in term of capital cost, operating cost, safety, space requirement and other factors.

<table>
<thead>
<tr>
<th>Table 3-2: Assumptions of PDU hydrogen supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow rate of H₂</td>
</tr>
<tr>
<td>Volume of H₂ consume</td>
</tr>
<tr>
<td>PDU maximum working time</td>
</tr>
<tr>
<td>Purity of H₂</td>
</tr>
</tbody>
</table>

**Hydrogen Gas Cylinder**

This option provides H₂ from hydrogen gas cylinders. It is convenient for direct delivery from Praxair Inc or other gas company. There are two cylinder sizes available for the industrial grade H₂: K size and T size cylinder contain the hydrogen volume of 196 ft³ and 261 ft³ which can support 1 hour and 1.4 hours supply time for PDU operation, respectively based on the use of 95 percent volume. Hence, 6 or 12 cylinders in package of gas cluster are needed for large volume H₂ requirement. Hydrogen K 6PK and Hydrogen T 12PK are chosen as two options for PDU H₂.
supply. Table 3-3 lists some parameters of Hydrogen K 6PK and Hydrogen T 12PK. Cost evaluation is presented in Table 3-4.

**Table 3-3: Parameters of two H₂ supply options (Hydrogen K 6PK and Hydrogen T 12PK)**

<table>
<thead>
<tr>
<th>Package mode</th>
<th>Volume</th>
<th>Supply time</th>
<th>Refill per month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen K 6PK</td>
<td>1176 ft³</td>
<td>6 hr</td>
<td>22 Clusters</td>
</tr>
<tr>
<td>Hydrogen T 12PK</td>
<td>3132 ft³</td>
<td>16.8 hr</td>
<td>8 Clusters</td>
</tr>
</tbody>
</table>

**Table 3-4: Cost evaluation of hydrogen gas cylinder systems**

<table>
<thead>
<tr>
<th>Package mode</th>
<th>Quotation</th>
<th>Delivery fee</th>
<th>Rental fee</th>
<th>Cost per month</th>
<th>Cost per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen K 6PK</td>
<td>$90</td>
<td>$20</td>
<td>$50/month</td>
<td>$2,470</td>
<td>$29,640</td>
</tr>
<tr>
<td>Hydrogen T 12PK</td>
<td>$254</td>
<td>$34</td>
<td>$96/month</td>
<td>$2,400</td>
<td>$28,800</td>
</tr>
</tbody>
</table>

H₂ supply system is expected to provide H₂ to the SHR process continuously. However, the refilling of gas clusters will cause the shutting down of H₂ supply system. Therefore, automatic switchover system is necessary to provide the continuous H₂ delivery. Fig 3-4 shows the schematic diagram of the Switchover system. It can provide automated switchover control and gas delivery up to ‘10’ cylinders.

**Figure 3-4: The schematic diagram of the switchover system**

Gas company also provides small size H₂ tank for costumes that need large hydrogen volume. It is called hydrogen on skid (seen in the picture above). Table 3-5 shows the parameters of
hydrogen skid system provided by Praxair Inc. Compared with hydrogen gas cylinder, this system has large hydrogen volume for one-month continuous H\textsubscript{2} supply.

Figure 3-5: Bulk Hydrogen Tank

Table 3-5: Parameters of hydrogen skid system

<table>
<thead>
<tr>
<th>System</th>
<th>skid size</th>
<th>H\textsubscript{2} volume</th>
<th>supply time</th>
<th>refill per month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen skid</td>
<td>14.5×5.5×5.5 ft</td>
<td>24,000 ft\textsuperscript{3}</td>
<td>136 hr</td>
<td>1 skid</td>
</tr>
</tbody>
</table>

The advantages of hydrogen skid include: high utilization rate, little maintenance requirement, a one-month continuous supply and lower cost for long-time running. However, the skid system requires an installation of fix to ground. And also it requires site survey approval and a 12 moth product supply agreement. The setup procedure is not easy and convenient compared with direct delivery of hydrogen gas cluster.

*Hydrogen Generator or on-site plant*

Hydrogen generators can produce pure hydrogen through the electrolysis of pure water. HGH series hydrogen generators series from Angstrom Advanced Inc are light, highly effective, energy-saving and environmentally friendly. Table 3-6 lists the total cost of hydrogen generator and on-site plant. The quotation is from Angstrom Advanced Inc.

Table 3-6: Cost evaluation of hydrogen generator and on-site plant

<table>
<thead>
<tr>
<th>System</th>
<th>Output Volume</th>
<th>Quotation</th>
<th>Operation fee</th>
<th>Cost per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Generator</td>
<td>176.6 ft\textsuperscript{3}/hr</td>
<td>$135,000</td>
<td>$104/month</td>
<td>$136,248</td>
</tr>
<tr>
<td>Hydrogen on-site plant</td>
<td>423.8 ft\textsuperscript{3}/hr</td>
<td>$165,000</td>
<td>$1040/month</td>
<td>$177,480</td>
</tr>
</tbody>
</table>
Generator or small on-site plant is good option for long-term program more than several years. This option can supply analysis grade H\textsubscript{2} with purity 99.99 percent.

Comparison of H\textsubscript{2} supply systems

Table 3-7 lists the cost evaluation of H\textsubscript{2} supply systems. The operating and investing costs were both included in this analysis. Investment cost was the major factor to determine the H\textsubscript{2} supply system for PDU process. Purchasing H\textsubscript{2} from gas delivery Inc. was chosen for the SHR PDU project. It was seen that the hydrogen on skid system has the lowest cost. However, site survey shows that it is unavailable to install the skid outside of CE-CERT lab building. Therefore, the hydrogen K cylinder in 6 packages with switchover system was used for of H\textsubscript{2} supply system in PDU process.

<table>
<thead>
<tr>
<th>Options</th>
<th>Total cost</th>
<th>Continuous supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switchover Hydrogen K 6PK</td>
<td>$29,640</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrogen T 12PK</td>
<td>$28,800</td>
<td>No</td>
</tr>
<tr>
<td>Hydrogen on skid</td>
<td>$26,040</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrogen generator</td>
<td>$136,248</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrogen plant</td>
<td>$177,480</td>
<td>Yes</td>
</tr>
</tbody>
</table>

3.4 Fluidized Bed Reactor Design

The project team chose the fluidized bed reactor in a bubbling-slugging fluidizing regime as the reactor for SHR process. In addition to their long history of being used as chemical process reactors and high heat transport rates, bubbling beds are also well-known for their reliability when used with biomass gasification. Residence time of the reactor is expected to be over 10 seconds. Longer residence time is favored because of slower gasification rate compared to partial oxidation reaction.

There are four parts in the reactor system: a fluidized bed reactor where the main chemical reaction occurs, a distributor that controls the gas inlet, a cyclone to collect sands that are taken out of the reactor by gas flow and a gas chamber.

Nominal reactor temperature of 750°C and pressure of 400 Pisa in the atmosphere of hydrogen and steam were chosen for the design basis. Silica sand provided by U.S Silica Company was used as inertia material in the fluidized bed. Other important physical properties are listed in Table 3-8 and Table 3-9. Sand is assumed to be uniformly spherical.
Table 3-8: Physical properties of silica sand in fluidized reactor

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>2.65</td>
</tr>
</tbody>
</table>

Table 3-9: Physical properties of hydrogen gas flow in fluidized reactor

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Density (g/cm³)</th>
<th>Viscosity (N-s/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>10.2</td>
<td>2.43E-4</td>
<td>1.90E-5</td>
</tr>
</tbody>
</table>

Symbols used in fluidized bed calculation is summarized below

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{mf}$</td>
<td>minimum fluidization velocity</td>
</tr>
<tr>
<td>$U_{ms}$</td>
<td>minimum slugging velocity</td>
</tr>
<tr>
<td>$U_t$</td>
<td>terminal fluidization velocity</td>
</tr>
<tr>
<td>$U$</td>
<td>fluidization velocity</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynold number</td>
</tr>
<tr>
<td>$Ar$</td>
<td>Archimedes number</td>
</tr>
<tr>
<td>$d_p$</td>
<td>solid particle diameter</td>
</tr>
<tr>
<td>$D$</td>
<td>reactor inner diameter</td>
</tr>
<tr>
<td>$D_B$</td>
<td>fluidization bubble diameter</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>gas density</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>solid density</td>
</tr>
<tr>
<td>$\mu$</td>
<td>gas viscosity</td>
</tr>
<tr>
<td>$H_L$</td>
<td>critical slugging bed height</td>
</tr>
<tr>
<td>$H_{mf}$</td>
<td>minimum fluidization bed height</td>
</tr>
<tr>
<td>$H_0$</td>
<td>minimum bed height</td>
</tr>
<tr>
<td>$H_{max}$</td>
<td>maximum bed height under fluidization velocity U</td>
</tr>
<tr>
<td>TDH</td>
<td>Transport disengagement height</td>
</tr>
<tr>
<td>$R_s$</td>
<td>ideal bed height</td>
</tr>
</tbody>
</table>

Reactor Dimension

The reactor is 14 feet in height with an outer diameter of 10.0cm and an inner diameter of 9.40cm. Calculation of fluidized bed height and gas velocity as well as some other important parameters is listed as follows:

Minimum fluidization velocity ($U_{mf}$)
U_{mf} is the minimum gas velocity that can support the particles in the reactor. Reynold number and Archimedes number are involved in the calculation of U_{mf} (Wen and Yu).

\[
Re_{mf} = \left[\left(33.7\right)^2 + 0.04084\pi\right]^{1/2} - 33.7 \quad (3-1)
\]

\[
Af = \frac{g^2 \rho_p \rho_g \phi_g^2}{\mu^2} \quad (3-2)
\]

\[
Re_{mf} = \frac{U_{mf} \rho_p \phi_p}{\mu} \quad (3-3)
\]

Thus we can obtain the value of U_{mf} through Eq. (3-3). Here U_{mf} = 0.019 m/s.

**Minimum slugging velocity (U_{ms})**

U_{ms} is the minimum superficial gas velocity for a slugging bed. As the size of bubbles grows, the wall of the reactor is playing greater roles on fluidization. Transition from a bubbling bed to a slugging bed begins when the bubble diameter reaches the reactor diameter. We use U_{ms} as the upper limit for fluidization velocity in our design. According to Baeyens and Geldart, if the bed height is lower than the critical bed height \(H_l = 1.3D^{0.175}\) (3-4) where bubble coalescence is complete,

\[
U_{ms} = U_{mf} + 0.07 \sqrt{gD} + 0.16(H_l - H_m)^2 \quad (3-5)
\]

If the bed height exceeds \(H_l\) then

\[
U_{ms} = U_{mf} + 0.07 \sqrt{gD} \quad (3-6)
\]

U_{ms} is the gas velocity at the transition to a slugging bed, which is the desired fluidization gas flow rate. Since longer residence time is preferred, we use Eq. (3-6) of the deeper bed model. Thus U_{ms} = 0.086 m/s.

**Terminal velocity (U_t)**

Terminal velocity is the maximum superficial gas velocity and it is also based on physical properties of sand and gas in the reactor (Souza - Santos). \(U_t\) is an important reference in fluidized bed design.

\[
U_t = \frac{4 \left(\rho_g - \rho_p\right)^2 \phi_p^2 \phi_g^2}{225 \rho_p \mu} \quad (3-7)
\]

\(U_t = 2.06\) m/s.

**Transport disengagement height (TDH)**

TDH is the vessel height required for disengaging larger particles from further upward movement.

\[
TDH = 9.55Ar^{0.5}Re^{0.75} \text{ (unit: m)} \quad (3-8)
\]
Ideal height = Rs \times (\text{bed height} + \text{TDH}) \times 1.2 \quad (3-9)

TDH = 0.08\text{m}. If ideal height is assumed to be 4.27\text{m} (total height of the reactor), H \leq 3.48\text{m}.

**Maximum slugging bed height**

According to Davidson and Harrison,

\[
\frac{0.711 (g Da)^{\frac{1}{2}}}{U - U_0} = \frac{H_0}{H - H_0} \quad (3-10)
\]

This could be rearranged into

\[
\frac{H_{\text{max}}}{H_0} = 1 + \frac{U - U_0}{0.35 \sqrt{g Da}} \quad (3-11)
\]

which is the ratio of maximum slugging bed height and origin bed height. Assuming that \(H_{\text{max}} = 4.27\text{m}\) at \(U = U_{\text{ms}}\), \(H_{\text{max}}/H_0 = 1.20\), \(H_0 = 3.56\text{m}\). But according to Eq. (3-9), bed height should be less than 3.48\text{m}. So we choose 3.48\text{m} as the final bed height design.

**Summary**

<table>
<thead>
<tr>
<th>Reactor inner diameter (cm)</th>
<th>Reactor total height (m)</th>
<th>Sand size (micron)</th>
<th>Bed height (m)</th>
<th>Bed pressure (atm)</th>
<th>Temperature (°C)</th>
<th>Gas velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.40</td>
<td>4.27</td>
<td>150</td>
<td>3.48</td>
<td>10.2</td>
<td>750</td>
<td>0.019-0.086</td>
</tr>
</tbody>
</table>

### 3.5 Computer Simulation of SHR Process

**Overview of Aspen plus**

ASPEN is a FORTRAN-based deterministic steady-state chemical process simulator developed by the Massachusetts Institute of Technology (MIT) for the Department of Energy (DOE) to evaluate synthetic fuel technologies. The ASPEN framework includes a number of generalized unit operation “blocks”, which are models of specific process operations or equipment (e.g., chemical reactions, pumps). By specifying configurations of unit operations and the flow of material, heat, and work streams, it is possible to represent a process plant in ASPEN. In addition to a varied set of unit operations blocks, ASPEN contains an extensive physical property database and convergence algorithms for calculating results in closed loop systems, all of which make ASPEN a powerful tool for process simulation.

ASPEN uses a sequential modular approach to flowsheet convergence. In this approach, mass and energy balances for individual unit operation blocks are computed sequentially, often in...
the same order as the sequencing of mass flows through the system being modeled. However, when there are recycle loops in an ASPEN flowsheet, stream and block variables have to be manipulated iteratively in order to converge upon the mass and energy balance. ASPEN has a capability for converging recycle loops using a feature known as “tear streams”.

In addition to calculations involving unit operations, there are other types of blocks used in ASPEN to allow for iterative calculations or incorporation of user-created code. These include design specifications and FORTRAN blocks. A design specification is used for feedback control. Any flowsheet variable or function of flowsheet variables can be set to a particular design value by the user. A feed stream variable or block input variable is designated to be manipulated in order to achieve the design value. FORTRAN statements can be used within the design specification block to compute design specification function values.

**SHR simulation**

All of the gaseous and liquid components used in the SHR simulation were described as distinct molecular species using Aspen’s own component properties database. Thermodynamics for the gasification and downstream unit operations are estimated by Peng–Robinson equation (PR) for high temperature, high pressure phase hydrocarbon behavior. The biosolid, biomass and ash components were modeled as non-conventional components using proximate and ultimate date to calculate the chemical and physical property.

The enthalpy model for the nonconventional components is HCOALGEN and the density model is DCOALIGN. The HCOALGEN model includes a number of empirical correlations for heat of combustion, heat of formation and heat capacity. All other values used were retrieved from the Aspen plus database. The whole simulation is controlled using FORTRAN routines (calculator blocks) and design specifications. Material, energy and carbon balances were given for each process unit and no detailed chemical kinetic models were considered in the simulation.

The SHRis simulated using decomposition and gasification units. These units are based on built-in Aspen reactor blocks and calculate the equilibrium composition in the reactor under the given conditions by means of Gibbs free energy minimization. The decomposition block converts the non-conventional feedstock into its basic elements, such as C (solid), H₂, O₂ and N₂, on the basis of yield information using the RYIELD block and the gasification block calculates the equilibrium product gas composition using the RGIBBS block.
Table 3-11: Feedstock composition in PDU test

<table>
<thead>
<tr>
<th>Proximate</th>
<th>Compound</th>
<th>Biosolid</th>
<th>Pine wood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile Matter</td>
<td>60.25</td>
<td>82.54</td>
</tr>
<tr>
<td></td>
<td>Fixed Carbon</td>
<td>10.00</td>
<td>17.17</td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>29.75</td>
<td>0.29</td>
</tr>
<tr>
<td>Ultimate</td>
<td>C</td>
<td>29.57</td>
<td>49.25</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>5.39</td>
<td>5.99</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>20.83</td>
<td>44.36</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5.79</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>1.56</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The fraction of leftover char is assumed as a function of gasification temperature only in the report. The char ratio is defined as the fraction of leftover char among the overall carbon in the feedstock. Based on the previous lab scale gasification test, the char ratio is set to be 35.2 percent, 17.9 percent and 9.2 percent with gasification temperature at 650°C, 750°C and 850°C, respectively.

The initial solid load in the slurry is 40 percent based on previous HTP test results. The total amount of H₂ injected in the system is defined as a function of total amount of carbon in the feedstock and the H₂/C molar ratio is set to be 1.0 all through the test. The carbon conversion efficiency is defined as fraction of the carbon in fuel gas (CO, CH₄ and C₂+) with expression given below.

\[
\text{Chemical Conversion Efficiency} = \frac{C_{\text{feedstock}} - C_{\text{CO₂}} - C_{\text{char}}}{C_{\text{feedstock}}}
\]

The mass and heat balance of the PDU operated under different temperature is given in Table 3-12 based on the simulation results.

Table 3-12: PDU mass and energy balance from simulation

<table>
<thead>
<tr>
<th>PDU performance</th>
<th>Operation temperature (°C)</th>
<th>650</th>
<th>750</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation pressure (psi)</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Slurry feed rate (lb/hr)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Slurry solid load</td>
<td>40%</td>
<td>40%</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>H₂/C molar ratio</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Char ratio (%)</td>
<td>35.2</td>
<td>17.9</td>
<td>9.2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Outlet gas</th>
<th>lb/hr</th>
<th>Vol%</th>
<th>lb/hr</th>
<th>Vol%</th>
<th>lb/hr</th>
<th>Vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.14</td>
<td>22.8%</td>
<td>0.22</td>
<td>34.3%</td>
<td>0.31</td>
<td>44.0%</td>
</tr>
<tr>
<td>CO</td>
<td>0.07</td>
<td>0.8%</td>
<td>0.34</td>
<td>3.8%</td>
<td>0.87</td>
<td>8.8%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.86</td>
<td>6.6%</td>
<td>1.31</td>
<td>9.2%</td>
<td>1.33</td>
<td>8.6%</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.47</td>
<td>9.8%</td>
<td>0.36</td>
<td>7.0%</td>
<td>0.16</td>
<td>2.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>3.17</td>
<td>59.4%</td>
<td>2.62</td>
<td>45.2%</td>
<td>2.26</td>
<td>35.4%</td>
</tr>
<tr>
<td>NH3</td>
<td>0.02</td>
<td>0.5%</td>
<td>0.02</td>
<td>0.5%</td>
<td>0.02</td>
<td>0.4%</td>
</tr>
<tr>
<td>H2S (PPM)</td>
<td>637</td>
<td>584</td>
<td>531</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical conversion efficiency (%)</td>
<td>40.0</td>
<td>44.3</td>
<td>52.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum heat requirement (kw)</td>
<td>2.0</td>
<td>2.5</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**SHR operation temperature and H2/C ratio impact**

H2/C molar ratio ranges from 0.5-3.0 with 0.5 interval is used to investigate the H2 impact on gas composition at different gasification temperature. The analysis is performed under the assumption that all the carbon in the product gases was present in the form of CO, CO2 or CH4. The mole percentages presented here are calculated using these three species only. Other components present in the product gas such as H2O and H2 are not included in the product mole percentage calculations. Hence, the mole percentages presented have been normalized to 100 percent based on the three carbon containing species, CO, CO2 and CH4, shown in Figure 3-6.

**Figure 3-6: Molar fraction of CH4, CO and CO2 at different gasification temperature**

It can be observed that the concentration of CH4 decreases with increasing gasification temperature whereas the concentration of CO and CO2 increases. This can be expected since the hydrogenation of carbon which is the primary CH4 generation reaction is mildly exothermic. The steam carbon reaction (2C+3H2O→3H2+CO+CO2) is endothermic. On the other hand, with H2/C increasing, the concentration of CH4 increases while the concentration of CO and CO2 decreases. This trend can be simply explained as the high concentration of H2 shifts the chemical equilibrium to its favorable side within the system that promotes the hydrogenation of carbon and restrains the formation of CO and CO2.
According to the simulation results, either increasing the H₂/C molar ratio or decreasing the gasification temperature can promote the CH₄ production in the SHR theoretically. In terms of H₂/C molar ratio, it must be ensure that the H₂ can sustain internal system cycle which also means no outside H₂ source is needed. Detail H₂ sustainability will be discussed in the pilot plant simulation section. For the gasification temperature effect, it is far more complicated in the really world than the simulation. Low temperature leads more leftover char and significant amount of tar will be generated that could block the pipeline and make the gas cleanup system more complex. Meanwhile, the low temperature also requires long residence time and adds the equipment cost, especially in large scale plant. After all, more research regarding optimum gasification temperature from biosolid and biomass comingle feedstock will be further investigated based on PDU test results.

### 3.6 Mass Flow Measurement Design for PDU

**Figure 3-7: Block Flow Diagram of Mass Flow Instrumentation for SHR process**

**Mass Flow Measure/Control System Overview**

SHR PDU process needstwo Mass Flow Controllers (MFC) in the process gas inlet and a Mass Flow Meter (MFM) in the product gas outlet of the reactor as shown in Figure 3-7.

*Specification of Two inlet mass flow controllers (one for H₂, the other for N₂):*

Operating pressure should be between 150 psi to 400 psi at room temperature. The nominal flow rate is 205 mol/h, or 76.5 Standard Liter Per Minute (SLPM).
Specification of Mass flow meter:

Operating pressure: Atmospheric. The nominal flow rate and gas composition are provided in the Figure 3-5 from heat and mass balance result. Coriolistype MFM can directly measure mass flow independent of gas types. Since the process uses a gas analyzer to measure the gas composition, signal from MFM can be correlated with the gas convection factor to get the real flow rate with following equations

\[
\text{Actual Gas Flow Rate} = \text{Output Reading} \times \frac{\text{Factor of the New Gas}}{\text{Factor of the Calibration Gas}}
\]

And the conversion factor of the gas mixture =

\[
\frac{100}{P_1 \times P_2 \times P_3}
\]

\[
\text{conversion factor}_1 \times \text{conversion factor}_2 \times \text{conversion factor}_3
\]

\[
P_1 = \text{percentage of gas 1 (by volume)} \quad \ldots
dots
\]

3.7 Gas Cleanup System and Steam Methane Reformer

Gas Cleanup System

The gasified product of any sulfur impurities in the feedstock will be hydrogen sulfide (H₂S), originally present in the feedstock in the form of elemental sulfur and organic sulfur. There will also be fine particulate matter, or fly ash, that is not removed by the lock hopper system in the product gas of the SHR.

A sulfur & particle trap (with a sorbent and a stainless steel frit filter) was installed in the product gas line, downstream of the SHR unit.

The sorbent used in the sulfur removal system is a zinc oxide pellet (G-72D) from Sud-Chemie, Inc. Zinc oxide (ZnO) reacts with hydrogen sulfide (H₂S) to produce zinc sulfide (ZnS) and water. The chemical reaction in between the zinc oxide and hydrogen sulfide can be summarized as below.

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}
\]

The physical properties of the sorbent and important design parameters are listed in Table 3-13.

<table>
<thead>
<tr>
<th><strong>Table 3-13: Characteristics of Sulfur Sorbent and Design Criteria</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zinc Oxide (ZnO) content (%)</strong></td>
</tr>
<tr>
<td><strong>Bulk density (g/cm³)</strong></td>
</tr>
<tr>
<td><strong>Surface area (m²/g)</strong></td>
</tr>
<tr>
<td><strong>Size (mm)</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>Void fraction (ε)</td>
</tr>
<tr>
<td>Total loaded mass (g)</td>
</tr>
<tr>
<td>Maximum Operating Temperature (K)</td>
</tr>
<tr>
<td>Nominal Operating Pressure (atm)</td>
</tr>
<tr>
<td>Life cycle @ 0.5% sulfur in feed stock</td>
</tr>
<tr>
<td>Outlet sulfur concentration</td>
</tr>
<tr>
<td>Maximum Space Velocity</td>
</tr>
</tbody>
</table>

The schematic diagram of the trap is shown in Figure 3-8. The entire trap was made of stainless steel tube (SUS 316) 50.8 mm (2.0”) OD and 1321 mm (52.0”) long enclosed by an electric heater (1.9 Kw). Additional thermal insulation was added with ceramic wool (Kaowool). The temperature of the trap was controlled by a PWM module. The sorbent was loaded inside the tube until the total stack height of sorbent was 23 inches. A fine particulate filter made of stainless steel frit, 27 inches long, was attached above (upstream of) the sorbent bed.

**Steam Methane Reformer (SMR)**

The catalyst for the SMR is nickel on an alumina supporting material (G90B, from Sud-Chemie, Inc.). It is in the form of cylindrical pellets with one center hole. The selection criteria for the steam reforming catalyst for the SHR process are as below:

- The catalyst is designed for the reforming of light hydrocarbons (less than C₃)
- The performance has been optimized for a low steam to hydrocarbon ratio (around 2.0 to 2.5)
- It has negligible pressure drop due to the physical shape of the catalyst

The detailed physical properties of the catalyst selected are listed in table 3-14.
The SMR is made of a seamless stainless steel tube (SUS 316), 1.0” OD, 0.75” ID and 65” long. Heat is provided by four sets of cylindrical electric heaters. Each heater is rated at 440W @ 120V and made of Inconel coil in an insulating gypsum block.
The catalyst was loaded inside of the tube to make a catalyst bed of 45.0” in length. The catalyst is supported by meshed stainless steel wool. The height of the meshed wool is 14.0”. The product gas from the SMR is cooled down to the room temperature via a heat exchanger, followed by steam trap for the continuous removal of condensate. The pressure of SMR, linked with the HGR, is controlled by a single backpressure regulator located downstream of the steam trap. Further details of SMR system including schematic diagram of the process is presented in the APPENDIX D part of this report.
Chapter 4: PDU Engineering

4.1 Lab Scale Batch Reactor Test for the Basic Design Parameter

Co-mingled feedstock of biomass and biosolids are used in SHR and experiments are carried out in inverted batch reactor to estimate the carbon conversion in the nominal temperature and pressure. Dimension of PDU was decided by the carbon conversion result obtained in this test.

Experiment conditions

Biomass is mixed with biosolids at defined water/carbon ratio (g/g). All of water source comes from moisture content in biosolids and total carbonaceous matter in feedstock is the sum of carbon in biomass plus carbon in biosolids. Experiment conditions are presented in the Table 4-1. And figure 4-1 shows the schematic diagram of the inverted batch reactor.

<table>
<thead>
<tr>
<th>Table 4-1: Experiment conditions for SHR of co-mingled feedstock and biomass feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass feedstock</td>
</tr>
<tr>
<td>Co-mingled feedstock</td>
</tr>
<tr>
<td>H₂O to carbon ratio</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Lab-scale reactor</td>
</tr>
</tbody>
</table>

Lab-scale batch reactor
**Batch Reactor Test Results**

Results from Proton Induced X-ray Emission analysis show that the biosolids contain main metal species including Fe, Ca, Al, Mg, K, Na, Cu as well as some other trace metals. The proposed hypothesis provides motivation to integrate metals in biosolids to catalyze the steam hydrogasification for a higher reaction rate instead of adding expensive commercial catalysts. The performances of steam hydrogasification reactions are evaluated to include kinetic parameters, carbon conversion. A first-order kinetic model based on the rate of gas generation is applied to determine the reaction rate of the individual gaseous product.

Fig 4-2 shows the carbon conversion of co-mingled feedstock and biomass feedstock only in the steam hydrogasification. There was 5 percent increase in the carbon conversion to gaseous products using co-mingled feedstock of pinewood and biosolids compared with using pinewood as the feedstock only. Table 4-2 presents the rate of product gas formation in steam hydrogasification using co-mingled feedstock and biomass feedstock only. The reaction rate of CH₄ and CO formation was enhanced using co-mingled feedstock of pinewood and biosolids compared with using biomass feedstock only.
4.2 Mock up test

Mock up test set up

The mock up test is to examine the fluidization performance and the viability of the PDU design. A 12-feet-high transparent plastic cylinder with the same inner and outer diameters as the real PDU is used as reactor. The test is controlled under atmospheric pressure and room temperature, using the same 150 micron silica sand as fluidization solids and air as flow gas. A U tube manometer with water is connected to the top of the reactor to measure the pressure drop during the fluidization.

Using the same formula (Eq. (1)-(6)), another series of gas flow rate based on the operation condition is obtained and tested. Bed height in the test is set to 1.83m (6 feet, half of the total height), which is higher than the critical height $H_c$ (0.860m). Summary of the test set up is listed in table 4-3.
Table 4-3: Fluidized bed mock up test operation condition

<table>
<thead>
<tr>
<th>Reactor inner diameter (cm)</th>
<th>Reactor total height (m)</th>
<th>Sand size (micron)</th>
<th>Bed height (m)</th>
<th>Bed pressure (atm)</th>
<th>Temperature (°C)</th>
<th>Gas velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.40</td>
<td>3.35</td>
<td>150</td>
<td>0.860</td>
<td>1</td>
<td>25</td>
<td>0.0863</td>
</tr>
</tbody>
</table>

Mock up test result

The sand begins to bubble very quickly. This is in accordance to the small \( U_{mt} \) value which can be deducted from Eq. (3-1)-(3-3) in Section 3.4 of this report. At the gas flow rate reaches 0.086m/s, the diameter of sand bubble approaches the cylinder diameter and the bubbles begin to burst. A bubbling-slugging bed is formed. Since the bed height reached the critical height, sand slugging is always in a stable axial plug flow state. The maximum bed height also fits the \( H_{max}/H_0 \) ratio obtained from Eq. (3-11), which is 1.20. A pressure drop of 127.4 Pa is observed during the fluidization. Actual photo taken from the mock-up test can be found in the APPENDIX D section of the report.

The result of the mock test shows that the bed performance predicted at the bubbling-slugging transition gas velocity based on previous calculation is reliable. As \( U_{mt} \) and \( U_{ms} \) is mostly related to physical properties of sand and reactor size only, the test result can prove that the design of a fluidized bed reactor with the same size under high temperature and pressure is also viable.

4.3 PDU Detailed Engineering

From the basic engineering data collected from section 4.1 & 4.2, research team started the detailed engineering with outside engineering firm. Technip USA Inc. (Claremont, CA) was chosen for the detailed engineering work. Technip USA is worldwide renowned engineering firm with the specialty in steam methane reforming and catalytic fluid cracking process, which has essential experience for the PDU design. Final outcome of the detailed design was presented in the APPENDIX D section of the report. Detailed fabrication drawings together with the design basis are presented.
Chapter 5:
PDU Operation Result

5.1 PDU test

*SHR test results*

Figure 5-1 shows performance of progressive cavity pump used in the PDU. Nominal designed flow rate of 5 lb/hr (40 ml/ min) was obtained at 20Hz of pump speed. Maximum flow rate of the feed pump was 80 ml/min @40 Hz, which is 200 percent of designed flow rate. In Figure 5-2, it also shows that the reactor can reach the desired temperature (650°C) at 200 percent designed flow rate.

![Figure 5-1: Steam pump (Hz) vs volume flow rate (ml/min)](image-url)
Figure 5-2: Reactor Temperature vs volume flow rate (ml/min)

![Graph showing reactor temperature vs volume flow rate.]

Figure 5-3: Temperature profile. Total recorded time was 5 hr. (2 hr per tick mark)

![Graph showing temperature profile.]

Figure 5-3 shown in above is the startup curve of PDU at nominal condition (20HZ). It took 4 hr to reach the desired temperature (650) of the reactor. Temperature profile at the steady state is shown in Figure 5-3. Upper 2 feet length section of the reactor reaches the desired temperature, while lower section of the reactor shows low temperature due to evaporation of the feedstock.
Figure 5-4: Temperature profile as a function of reactor height (Distance from Top)

Figure 5-4 shows the reactor can hold the desired temperature up to 200 percent of nominal flow rate.

*Gas Cleanup System test results*

**Figure 5-5: Gas Cleanup System Test Run**

- Temperature: 600 °F
- SV (hr⁻¹): 33000
- PS (µm): 150 <dp< 250
- H₂S concentration [inlet] (ppm): 2000

- Breakthrough conc. for protecting SMR catalyst @ 750 °C
- Breakthrough conc. for protecting FT catalyst

Run 3 (no steam) — Run 8 (30 vol % steam)
Figure 5-5 shows the operation result of gas cleanup system. The result shows the effective cleanup of sulfur species (H₂S) at the elevated temperature (600°F) to less than 1 ppm. The result also shows the presence of the steam in the SHR producer gas does not affect the performance of cleanup sorbent. Presence of the steam only affect the break-through time of the sorbent. With the steam, which is the typical condition of SHR producer gas, 15 percent Reduction of sorbent life time is expected.

**PDU Operation Result (SHR + Gas Cleanup + SMR)**

In Figure 5-6 shows operation of PDU at the nominal designed rate with combination of gas cleanup system and SMR for the pretreated feedstock with HTR process. For the 1st 1 hour of PDU operation, only SHR part of was operating. After SHR reach the steady state (Time mark around 15:29), SMR section of the PDU was started. It shows PDU system is producing 3:1 ration of H₂ and CO when it reaches the steady state (Time mark after 16:48).
Table 5-1: Summarizes measured performance of PDU in final state

<table>
<thead>
<tr>
<th></th>
<th>SHR only (Task 3)</th>
<th>SHR + SMR (Task4)</th>
<th>Target (Task 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product gas yield</td>
<td>1.5 m³ (~1.5kg,</td>
<td>1.5 m³ (~1.5kg,</td>
<td>&gt;1200 kg / ton</td>
</tr>
<tr>
<td></td>
<td>wet)/kg feed</td>
<td>wet)/kg feed</td>
<td>of feed</td>
</tr>
<tr>
<td>Energy Content</td>
<td>14 MJ / kg feed</td>
<td>15 MJ / kg feed</td>
<td>&gt;12 GJ/ ton of</td>
</tr>
<tr>
<td>H₂</td>
<td>55Vol%</td>
<td>65Vol%</td>
<td>50-80Vol%</td>
</tr>
<tr>
<td>CO</td>
<td>10Vol%</td>
<td>22Vol%</td>
<td>15-30 Vol%</td>
</tr>
<tr>
<td>CH₄</td>
<td>30Vol%</td>
<td>3Vol%</td>
<td>&lt; 5Vol%</td>
</tr>
<tr>
<td>CO₂</td>
<td>5Vol%</td>
<td>10Vol%</td>
<td>5-20Vol%</td>
</tr>
<tr>
<td>Sulfur, Tar, NH₃</td>
<td>n/a</td>
<td>n/a</td>
<td>&lt; 0.01 ppm</td>
</tr>
</tbody>
</table>
Chapter 6: Pilot Plant Design

6.1 Pilot plant modeling

A 5 ton per day steam hydrogasification pilot plant is designed and simulated with downstream Water Gas Shift (WGS) unit that converts CO into H₂ and CO₂ at the presence of steam. The WGS unit is simulated using Aspen equilibrium blocks and calculate the chemical equilibrium inside the reactor at the given temperature and pressure. CO conversion higher than 85 percent can be achieved based on the simulation results. The whole process schematic flow diagram is given in Figure 6-1.

![Figure 6-1: Schematic of SHR with WGS](image)

System H₂ availability is discussed in detailed in this section with definition given below.

\[ \text{H₂ availability} = \frac{\text{H₂ Recycle}}{\text{H₂ In}} \times 100 \]

In order to sustain an internal H₂ cycle between SHR inlet and WGS outlet, the H₂ availability must be higher than 100. H₂ availability at pilot scale gasifier operated at 650°C, 750°C and 850°C is given in Fig.2 with initial H₂/C molar ratio ranges from 0.5-3.0.
Based on the simulation results, any point below the dash line is considered as unfavorable and cannot make the system self sustainable. The maximum H₂/C molar ratio that meets the system H₂ internal cycle at different gasification temperature is given in Table 6-1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>650</th>
<th>750</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max H₂/C molar ratio</td>
<td>0.8</td>
<td>2.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Mass and energy balance of pilot plant with maximum H₂/C molar ratio at 650°C, 750°C and 850°C is given in Figure 6-3, Figure 6-4 and Figure 6-5, respectively. The heat requirement in gasifier, gas cooling system, WGS unit and steam condensing is calculated in the unit of kw. It should be noticed that the number in minus represents heat is imported into the system while vice versa.

Other deliverables in Task#5 such as Block Flow Diagram, Process & Utility Flow Diagrams, Plant Layouts & Equipment together with the Estimated Project Cost can be found in the APPENDIX F section of the report.

Process economic analysis was established for a 3500 BDT/day SNG plant using biosolid and green waste as feedstock. Based on the analysis result, the SNG production cost is 4.39 $/MMBTU with an IRR of 16.68 percent while feedstock cost and feedstock delivery cost are not taken into consideration. The detail of the analysis is also provided in the APPENDIX G.
Figure 6-3: Mass and heat balance of pilot plant with gasification temperature at 650°C

Figure 6-4: Mass and heat balance of pilot plant with gasification temperature at 750°C
Figure 6-5: Mass and heat balance of pilot plant with gasification temperature at 850°C
Chapter 7: Summary of Results

All of the major technical objectives of this project were met. This section will summarize the results.

A PDU scale HTP was designed, built and demonstrated. The HTP produced a pump-able feedstock of comingled biomass and biosolid and met all of the target specification described in the performance objective. The most important result is that a feedstock of up to 40 percent solid loading can be converted into the pump-able form with this technology.

A PDU scale SHR process was also designed, built and successfully operated. A Gas Cleanup system and SMR were developed separately and integrated with the SHR reactor. The production of syngas with all the target specifications was successfully demonstrated. The Syngas production rate is 1.5 cubic meters per kilogram input of feed. The energy content of the producer gas was 15MJ per kilogram input of feedstock. The production of synthesis gas at the temperature range of 650-750°C, a H2/C mole ratio of 1.0 and H2O/feedstock mass ratio of 2 was successfully demonstrated.

A preliminary design of a pilot plant at 5 tons per day capacity using the PDU technology was completed. A block flow diagram with process mass and energy balance and process and utility flow diagrams was developed as a major deliverables of the project.

Preliminary process economic analyses were completed for a 3500 BDT/day SNG plant using biosolids and biomass as feedstock. It was estimated that the SNG production cost is 4.39 $/MMBTU with an IRR of 16.68 percent. This result together with the preliminary design basis for the pilot plant provides the confidence for moving forward to the pilot plant demonstration of this technology at the site of waste treatment plant.
GLOSSARY

BDT ........................................ Bone Dry Tonne
CEC ........................................ California Energy Commission
CE-CERT .................................. College of Engineering-Center for Environmental Research and Technology
CH₄ ........................................ Methane
CO .......................................... Carbon Monoxide
CO₂ ........................................ Carbon Dioxide
DAFT ...................................... Dissolved Air Floatation Thickener
DOE ......................................... Department of Energy
FT Fischer-Tropsch
GC Gas Chromatography
GC-FID .................................. Gas Chromatography with Flame Ionization Detector
GC-TCD .................................. Gas Chromatography with Thermal Conductivity Detector
H₂ ............................................. Hydrogen
HTP ........................................ Hydrothermal Pretreatment
HTR ........................................ Hydrothermal Reactor
H₂C .......................................... Ethylene
H₂S ........................................ Hydrogen Sulfide
Hz ............................................ Hertz
MAWP ..................................... Maximum Allowable Water Pressure
MAWT ..................................... Maximum Allowable Water Temperature
MAWL ..................................... Maximum Allowable Water Loading
MFC ......................................... Mass Flow Controller
MFM ......................................... Mass Flow Meter
MIT ......................................... Massachusetts Institute of Technology
mm .......................................... Millimeter
NiO .......................................... Nicole Oxide
NH₃ ....................................................... Ammonia
PDM ..................................................... Pressure Display Module
PDU ...................................................... Process Demonstration Unit
PPM ..................................................... Parts Per Million
PR Peng-Robinson
RPM ..................................................... Round Per Minute
PWM .................................................... Pulse Width Modulation
SHR ....................................................... Steam Hydrogasification Reaction
SLPM ..................................................... Standard Liter Per Minute
SNG ....................................................... Substituted Natural Gas
SMR ....................................................... Steam Methane Reforming
SOP ....................................................... Standard Operation Procedure
SVM ....................................................... Solenoid Valve Module
TPD ....................................................... Tone Per Day
TDH ....................................................... Transport Disengagement Height
UC University of California
USA ....................................................... United State of America
WGS ....................................................... Water Gas Shift
ZnO ....................................................... Zinc Oxide
ZnS ....................................................... Zinc Sulfide